

## TEMPORARY STORAGE OF IONS FOR MASS SPECTROMETRIC ANALYSES

The invention relates to methods and devices for the temporary storage of ions which are to be subjected to mass spectrometric analysis. Such temporary storage of ions in an RF multipole rod system for their analysis in an RF quadrupole ion trap is known from U.S. Pat. No. 5 179 278.

The invention uses this known temporary storage for such ions which are produced in an ion source from substance peaks from chromatographic or electrophoretic separation devices, or from other devices which feed substances in form of short-lasting peaks. The temporary store thereby accepts sufficient ions of a substance peak for several successive mass spectrometric analyses, so that a mass spectrometric characterization of the substances, which may also require varying measurement methods, is made possible to the desired degree.

Particularly ions from electrophoretically or chromatographically separated substance peaks should be able to be temporarily stored long enough until the mass spectrometric analyses have been concluded to the desired extent. Several temporary stores can collect the ions from several rapidly successive substance peaks. However, short-lasting substance peaks from laser desorptive or pyrolytic processes can also be thoroughly analyzed by means of temporary storage.

### PRIOR ART

The storage of ions in RF quadrupole rod systems has been known in principle since the time of invention of this principle by Wolfgang Paul.

An application of this storage is described in U.S. Pat. No. 5 179 278. Here, ions from an ion source are temporarily stored before their analysis in an RF quadrupole ion trap in an RF multipole rod system. On the RF multipole rod system, apertured diaphragms with reflecting electric potentials were attached at both ends for the storage of ions. The temporary storage serves to collect ions even during that time period in which the ion trap is being used for the analysis of ions, and therefore cannot accept any ions. In this way the degree of temporal utilization of the ion source as well as the ion trap is increased. In U.S. Pat. No. 5 179 278 it has been estimated by calculation of the storage capabilities of RF multipole ion traps and RF quadrupole rod systems that, depending upon the design of the rod system, the ions can be temporarily stored for much more than just one filling of the ion trap in the rod system. It is however expressly emphasized that "there is little point in collecting more than the  $1.1 \times 10^7$  ions that the ion trap can accept" (Column 5, Line 22 ff).

The unfiltered temporary storage of ions does not however provide any significant improvement, as has already been described in U.S. Pat. No. 5 179 278 by numerical examples, since under favorable circumstances with this method a maximum improvement in the degree of utilization of ion sources or ion traps by a factor of two results, as can be seen in the following example: if the ion source supplies such a minimal ion current that the filling time of the ion trap lasts much longer than the analysis period in the ion trap, the temporary store does not practically represent an improvement since hardly anything is gained by collection during the analysis time. If the ion source provides such a large ion current that the filling time is very short in comparison to the analysis period, there is again no improvement since collection during the analysis time makes no sense. Collection of ions during analysis is sensible only if the filling period

is about the same as the analysis period. In order to improve this by a factor of two, yet another condition must be fulfilled in which the ion trap can be filled very quickly from the temporary store. Only if this filling time from the temporary store is very short in comparison to the analysis period, can utilization be improved by the maximum possible factor of two.

It is however the case that RF quadrupole ion traps work extremely quickly nowadays. In the mass range of up to 500 atomic mass units, a spectrum can be scanned in about 15 milliseconds. Even for the mass range reaching to 2,000 atomic mass units, which is of particular interest for biochemical problems today, the ion trap can work with analysis times of about 100 milliseconds. On the other hand, the filling of the ion trap from the RF multipole rod systems used as a temporary store, as already indicated in U.S. Pat. No. 5 179 278, takes several tens of milliseconds, and is therefore certainly comparable with the ion analysis times.

These ratios can also be seen in the numerical examples given in U.S. Pat. No. 5 179 278 and were therefore also known to the inventor. The usefulness of temporary storage in U.S. Pat. No. 5 179 278 is also primarily seen in the ability to filter out undesirable ions in the temporary store. The main claims are therefore already formulated in such a way that only desirable ions are to be temporarily stored and undesirable ions excluded from storage. Various methods are used for the filtration of desirable ions. Only by means of this temporary storage filter is the utilization ratio significantly increased. (At the time of invention U.S. Pat. No. 5 179 278, it was not yet known that undesirable ions could also be filtered out during the filling process of ions in the ion trap.)

For the ions from such ion sources as are located outside the vacuum system, and the ions of which are fed into the vacuum system, the RF multipole rod system can also be used for the thermalization of ions accelerated during the introduction, as described in U.S. Pat. No. 4 962 736. It is true that U.S. Pat. No. 4 962 736 is limited to application in quadrupole mass spectrometers, however it is obvious that this method can also be used for other mass spectrometers which work with ions of uniform kinetic energy.

Temporary storage and thermalization can however not only be done in RF multipole rod systems. The author of the present patent application introduced a new class of ion-optical systems in patent application U.S. Ser. No. 08/565 107 at the United States Patent and Trademark Office which can be used as guidance systems, storage systems and thermalization systems. The text describing this application is to be included here completely.

With the exception of the patent cited, the possibility of temporary ion storage has not been further pursued until now, although systems for the thermalization and guidance of ions have become more widespread in the meantime and have been applied in commercial mass spectrometers of various types since the beginning of this year.

On the other hand, suiting mass spectrometric measurement methods to the increasingly briefer substance peaks of modern substance separation methods has remained an unsolved mass spectrometric problem. Separation methods such as capillary electrophoresis and liquid chromatography with microcapillary columns are being developed for time-saving reasons into faster and faster methods. Nowadays they provide the separated substances in peaks which only last a few 10 to 100 milliseconds. Mass spectrometry is just barely in a position to provide summary spectra of the substances from the substance peaks.